GAS CHROMATOGRAPHIC INVESTIGATION OF ORGANOSILICON COMPOUNDS WITH SPECIAL REFERENCE TO TETRAALKYL- AND TETRAALKOXYSILANES

INGA-BRITT PEETRE

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av

Inga-Britt Peetre

Civ.ing., Mlm

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Inga-Britt Peetre, Department of Technical Analytical Chemistry, The Lund Institute of Technology, Chemical Center, P.O. Box 740, S-220 07 Lund 7, Sweden.

The thesis consists of a summary and the following papers. In the summary these papers will be referred to by the capital letters A-F.

A. I.-B. Peetre. A Method and Program for Accurate Determination of Kováts' Retention Indices with Special Reference to Multicomponent Mixtures. Chromatographia 6 (1973) 257.

B. O. Ellrén, I.-B. Peetre and B.E.F. Smith. Gas Chromatographic Investigation of Organometallic Compounds and their Carbon Analogues. I. Determination, Calculation and Correlation of Kováts' Retention Indices for Tetraalkoxysilanes. J. Chromatogr. In press.

C. I.-B. Peetre. Gas Chromatographic Investigation of Organometallic Compounds and their Carbon Analogues. II. Improved Method for Calculating Retention Indices of Tetraalkoxysilanes. J. Chromatogr. In press.

D. I.-B. Peetre. Gas Chromatographic Investigation of Organometallic Compounds and their Carbon Analogues. III. A Study of Kováts' Retention Indices for Tetraalkoxysilanes Containing Branched Alkoxy Groups. J. Chromatogr. In press.

E. I.-B. Peetre and B.E.F. Smith. Gas Chromatographic Investigation of Organometallic Compounds and their Carbon Analogues. IV. Determination, Calculation and Correlation of Kováts' Retention Indices for Tetraalkylsilanes. J. Chromatogr. In press.

F. O. Ellrén, I.-B. Peetre and B.E.F. Smith. Gas Chromatographic Investigation of Organometallic Compounds and their Carbon Analogues. V. Use of Refractive Index in Conjunction with Kováts' Retention Index for the Identification of Organosilicon Compounds. J. Chromatogr. In press.

S U M M A R Y

INTRODUCTION

Gas chromatography has been used for some 20 years for the separation and determination of all types of organic compounds. Much of the interest has been focused on hydrocarbons because of the technical importance of this type of compound and the difficulty encountered in their analysis. While the early work dealt mainly with the solution of separation problems in connection with the more common types of organic compounds, the center of attention has gradually shifted to more unusual types and to such fields as trace analysis, identification of separated compounds and calculation and correlation of retention parameters. The present investigation belongs to the two last-mentioned fields in that it mainly concerns methods for accurate determination and calculation of Kováts' retention indices and studies of interrelations between retention indices as well as relations between retention indices and other physical quantities. In the following survey the fundamental themes dealt with in this thesis are summarized.

1. Accurate determination of Kováts' retention indices for multicomponent mixtures (A).
2. Calculation of retention indices for mixed tetraalkoxy- and mixed tetraalkylsilanes from retention indices of their symmetrical counterparts (B-E).
3. Relations between retention indices and carbon numbers for homologous and other series of tetraalkoxy- and tetraalkylsilanes (B,E).
4. Relations between retention indices for homologous series of mixed tetraalkoxy- or mixed tetraalkylsilanes on the one hand and retention indices for their symmetrical counterparts on the other (B, C, E).
5. Two-phase plots for retention indices measured on a nonpolar stationary phase (Apiezon) and a polar phase (XE-60) and two-temperature plot for retention indices measured on Apiezon L (B-E).
6. Relations between retention indices of tetraalkyl- and tetraalkoxysilanes (E).

7. Calculation of temperature dependence of retention indices for mixed tetraalkoxysilanes and for tetraalkylsilanes (B, C, E).
8. Calculation of boiling points from retention indices (B, E).
9. Use of refractive index in conjunction with retention index for the identification of organosilicon compounds (F).
10. Identification of tetraalkoxy- and tetraalkylsilanes by gas chromatography and refractometry (B-F).

PREVIOUS WORK

Previous gas chromatographic investigations in the organosilicon field of interest are to a large extent of the retention data collecting type with little or no subsequent treatment of the data. In several investigations dealing with tetraalkylsilanes the main object was to study the redistribution of alkyl groups around the silicon atom in the presence of catalysts and not the determination of retention values. Accordingly, it seems justified to state that the organosilicon field of interest is up to now on the whole virgin soil as far as more thorough studies in gas chromatography are concerned. The literature covering gas chromatographic investigations of tetraalkoxy- and tetraalkylsilanes is discussed in papers B and E.

EXPERIMENTAL

Apparatus and columns. Most of the work was performed using a Varian gas chromatograph model 1400 with flame ionization detector. Since the temperature scale on this instrument could not be read to better than $\pm 1^{\circ}C$, an auxilliary thermocouple and temperature gauge was used which permitted measurement of the temperature to $\pm 0.1^{\circ}C$ (Mettler TM15). The temperature was constant within this range during a measurement. Any significant deviation of the observed temperature from the measurement temperature in the tables was corrected for.

In this work either packed columns (B, C, D) or capillary columns (C, E) were utilized.

Packed columns. Steel columns (0.3 - 6 m × 1/8" o.d.) were packed with either Apiezon M, Apiezon L or cyanosilicone GE-XE-60, 4 and 5% by weight, respectively, on acid washed and DMCS-treated Chromosorb G, 80-100 mesh. The column length was chosen to give a maximal retention time of about one hour. The carrier gas was nitrogen at about 30 ml/min.

Capillary columns. Perkin-Elmer steel columns (50 m × 0.25 mm) containing Apiezon L or cyanosilicone XE-60 were used.

Materials. All compounds investigated were prepared in this laboratory. Among the several methods used those formulated below were preferred.

Tetraalkoxysilanes (B, C, D)

Symmetrical: $SiCl_4 + 4\ ROH \rightarrow Si(OR)_4 + 4\ HCl$

Mixed: $Si(OR)_4 + 2\ R'OH \xrightarrow{HCl} (RO)_nSi(OR')_{4-n} + 2\ ROH$

The molar proportions between the tetraalkoxysilanes obtained in the last case are approximately 10-20-40-20-10 for n = 0-4, respectively.

Tetraalkylsilanes (E)

Symmetrical: $SiCl_4 + 4\ RLi \rightarrow SiR_4 + 4\ LiCl$

Mixed: $SiR_4 + SiR'_4 \xrightarrow{AlCl_3} R_nSiR'_{4-n}$

The molar proportions between the tetraalkylsilanes obtained in the "mixed" synthesis are the same as for the tetraalkoxysilanes.

The syntheses were performed on a small scale. No separations of the compounds formed were made prior to the gas chromatographic investigation. The peaks in a chromatogram resulting from mixed silanes could generally be unequivocally assigned, since the various silanes resulting from the systematic exchange of one alkoxy or one alkyl group for another appeared in the order of increasing molecular weight on both the stationary phases.

1. ACCURATE DETERMINATION OF KOVÁTS' RETENTION INDICES FOR MULTICOMPONENT MIXTURES (A)

The preferred and recommended method for recording retention data in

gas chromatography is in terms of Kováts' retention indices[1]. The Kováts' system is based on the approximate linear relation between the logarithm of the adjusted retention time and the carbon number of n-alkanes. In practice the substance whose retention index is to be determined is mixed with two bracketing consecutive n-alkanes and the mixture chromatographed. The retention index of the substance (I) is then found by logarithmic interpolation of the adjusted retention time (t'_r) between those of the two alkanes (t'_n and t'_{n+1}) whose retention indices are defined as 100 times their carbon numbers (n and n+1).

$$I = 100n + 100 \frac{\ln t'_r - \ln t'_n}{\ln t'_{n+1} - \ln t'_n} \qquad (1)$$

This methodology ensures a high degree of accuracy, since the substance and the alkanes are always eluted in close sequence.

If the retention indices of several compounds in a mixture are desired, it is often not possible to bracket each substance by two consecutive n-alkanes because overlapping of peaks is difficult to avoid. On the other hand, to use alkanes other than consecutive ones when calculating retention indices is not recommended[2]. To circumvent this problem one can run the compound mixture and the alkane mixture separately, but then there is always a certain risk involved with changing conditions between the runs, which may lessen the accuracy of the retention values obtained. A FORTRAN program for calculating retention indices using the above method has been given by Castello and Parodi[3]. However, this program is not intended for automatic operation and furthermore not applicable to the calculation of accurate retention indices.

The method described in paper A was developed in order to solve the problem outlined above. It permits the determination of accurate retention indices without the need for bracketing each compound by two consecutive n-alkanes. A further merit of the method is that it makes possible good control of the column conditions and permits a correlation of the retention time with the amount of substance injected. In the following the main steps in the method are described.

Standard runs. A mixture containing a series of consecutive n-alkanes covering the retention index range of interest is chromatographed several times. The mean values of the natural logarithms of the adjusted retention times are calculated and used as standard values for a certain column at a certain temperature.

Analysis runs. At least three n-alkanes, evenly distributed over the expected retention index range, are added to the compound mixture and the resulting mixture chromatographed a few times on the same column and at the same temperature as above. The natural logarithms of all adjusted retention times are calculated.

Regression analysis. Corresponding values of n-alkanes in the standard and analysis runs form xy-pairs, from which a linear equation is derived by regression analysis. The slope of the line affords a control of the equality between the standard and analysis runs.

Conversion of analysis values to standard values. All analysis values are converted to standard values by use of the equation above. This means that every compound is bracketed by two consecutive n-alkanes, whose $\ln t'_r$ values are known with good precision.

Retention indices for each analysis run are calculated for all substances of the compound mixture and the mean value and mean deviation of the retention index is calculated for each substance.

Correction of retention index for amount of substance injected. When high-boiling compounds are run at a temperature lower than optimal, fronting may result on some stationary phases. Under such conditions the retention index value will depend on the amount of substance injected. A possibility to calculate the retention index corresponding to an injected amount equal to zero is provided in the method.

FORTRAN program. The calculation is done using a FORTRAN program which is adapted to automatic operation. A detailed description of the program is given in paper A.

Accuracy of retention indices. The accuracy with which a retention index can be determined, using the present method, depends mainly on errors in the retention time measurement. The retention time was measured to 0.1 sec. by means of a slope detector constructed at this laboratory[4]. This high precision in the retention time measurement makes it probable that retention indices on a XE-60 capillary column at 140°C in the range above 900 may be determined to one decimal place, while retention indices below 700 should be given as integers. In the range between 700 and 900 the accuracy is intermediate.

Application of the method. The computer method outlined above was applied to the calculation of retention indices in the investigations described in papers C, D and E. In the case of paper B it was used only to a minor extent, since the main part of this investigation was completed before the computer method was worked out.

2. CALCULATION OF RETENTION INDICES FOR MIXED TETRAALKOXY- AND MIXED TETRAALKYLSILANES FROM RETENTION INDICES OF THEIR SYMMETRICAL COUNTERPARTS (B-E)

The calculation of retention indices for mixed silanes from retention indices for their symmetrical counterparts is to a first approximation based on the assumption of additive group retention indices. The group values are obtained from retention indices of symmetrical silanes by division by four. This simple method was applied to tetraalkylsilanes by Semlyen and Phillips[5], but with little success.

$$I(R_4Si) = \Sigma I(RSi) \qquad (2)$$

It is obvious that a correction which takes into account the deviation from additivity of the group retention indices in the mixed silanes is necessary. One method for calculating this correction is presented in eqn. 3, and is valid for tetraalkoxysilanes. Another method is described by eqn. 5.

$$I(RO)_4Si = \Sigma I(RO)Si + \underbrace{\Sigma(n \cdot d \cdot k)_{RO-RO}}_{\text{correction term}} \qquad (3)$$

In this expression,

RO denotes a normal alkoxy group;

I(RO)Si = group retention index;

n = combination number (see B, p. 5);

d = carbon number difference between combined alkoxy groups;

k = constant dependent on the smallest alkoxy group in a combination.

The correction term in eqn. 3 expresses the deviation from additivity of the group retention indices, I(RO)Si, in mixed tetraalkoxysilanes very accurately as can be seen from B, Table II, where the experimental and calculated retention indices are given.

When the same equation was applied to mixed tetraalkylsilanes (E)

$$I(R_4Si) = \Sigma I(RSi) + \Sigma(n \cdot d \cdot k)_{R-R} \qquad (4)$$

it appeared that certain limitations in its utilization existed in that the deviation between experimental and calculated values for tetraalkylsilanes containing Me groups bonded to silicon was considerably greater than for other types of tetraalkylsilanes (see E, Table I).

The reason for the different behaviour of tetraalkyl- and tetraalkoxysilanes, in which latter case the equation fitted all types of compounds, is to be sought in their different structures. In tetraalkoxysilanes, $(RO)_4Si$, the alkyl groups are isolated from the central silicon atom by an oxygen atom, while in the tetraalkylsilanes, R_4Si, the alkyl groups are bonded directly to the silicon atom. This influences the CH_3 group most while longer alkyl groups may be considered to be isolated from the silicon atom by the innermost CH_2 group, making them equivalent with the alkoxy groups.

This argument is partly founded on a proposed theory, which attempts to explain the deviation of the group retention indices, I(RO)Si, from additivity in mixed tetraalkoxysilanes (see B, p. 8-9). It is assumed that

an interaction takes place between certain CH_3 and CH_2 groups in a mixed tetraalkoxysilane and it is shown that the correction term in eqn. 3 may be obtained by adding a number of increments arising from this interaction.

For a more accurate calculation of retention indices of mixed tetraalkylsilanes containing Me groups, which is based on a linear relation between their retention indices and the retention indices of the corresponding tetraalkoxysilanes, see part 6 of the summary.

In eqn. 3 the correction term was given as $\Sigma(n \cdot d \cdot k)$, where d is the carbon number difference between combined alkoxy groups. Although this expression describes the deviation of the sum of the group retention indices from additivity rather accurately, it was found possible, by exchanging d for the difference between two retention indices, to calculate the correction term with still better precision.

$$I(RO)_4Si = \Sigma I(RO)Si + \Sigma n[k'I(R'O)_4Si - k''I(R''O)_4Si] \qquad (5)$$

In this expression,

OR' and OR'' = alkoxy groups in a combination (R' > R'');

k' and k'' are constants dependent on the smallest group present in a combination.

Eqn. 5 was derived from a linear relation existing between retention indices for homologous series of mixed tetraalkoxysilanes and those of their symmetrical counterparts, as described in C and part 4 of the summary. That eqn. 5 is superior to eqn. 3 for calculating retention indices for mixed tetraalkoxysilanes is evident from C, Table I. Here the experimental values for 21 mixed tetraalkoxysilanes accurately measured on an Apiezon L capillary column are given and compared with those calculated by eqns. 3 and 5. The mean deviation between experimental and calculated values is 0.5 index units for eqn. 5 and 1.2 index units for eqn. 3. Similar results were obtained for the XE-60 capillary column (see C, Table II).

Although a linear relation exists between retention indices for homologous series of mixed tetraalkylsilanes and retention indices of their symmetrical counterparts, no general expression similar to that in eqn.

5 can be derived from this fact. The reason for this is the absence of any relation between the constants in the linear equations valid for the three homologous series $R_xSiR'_{4-x}$ (x = 1-3), e.g. Me_3SiR', $Me_2SiR'_2$, Me_3SiR'. (See further E, p. 8-9 and Table VI and part 4 of the summary).

The tetraalkyl- and tetraalkoxysilanes hitherto discussed all contain only normal alkyl and alkoxy groups. In order to study the application of eqn. 3 to some other types of silanes a number of tetraalkoxysilanes containing branched alkoxy groups was prepared and their retention indices determined. Surprisingly enough, eqn. 3, which was developed for normal tetraalkoxysilanes, holds good also for some tetraalkoxysilanes with branched alkoxy groups (see D, Table II). Thus, this was the case for tetraalkoxysilanes with i-PrO and i-BuO groups on Apiezon M and for tetraalkoxysilanes with i-BuO groups on XE-60. On both phases compounds with s-BuO groups exhibited poor agreement between experimental and calculated values.

No attempts have been made to investigate whether equations for calculating retention indices of mixed tetraalkylsilanes with normal alkyl groups also fit compounds with branched groups. However, for several reasons, among them the increased crowding around the silicon atom, it is believed that this will not be the case.

Some concluding remarks will be made about the calculation of ΔI-values. Since the ΔI-values are obtained by subtracting I^{Ap}_{160} from I^{XE}_{160}, both of which may be calculated, there is no real need for equations for calculating this quantity. However, in one instance, viz. in the case of normal tetraalkoxysilanes, an equation was given (see B, eqn. 3). It shows that group ΔI-values for tetraalkoxysilanes are additive except for ΔI(MeO)Si, where a correction has to be made.

3. RELATIONS BETWEEN RETENTION INDICES AND CARBON NUMBERS FOR HOMOLOGOUS AND OTHER SERIES OF TETRAALKOXY- AND TETRAALKYLSILANES (B, E)

For a long time it has been known that there exists a linear relationship between retention index and carbon number for homologous series

of compounds, with the exception of the first members in a series. In fact this relation was established already in the first paper published on gas chromatography by Martin and James[6] in 1952.

For normal tetraalkoxysilanes a linear relationship between retention index and carbon number exists for any homologous series, e.g. for $(RO)_3SiOC_nH_{2n+1}$, counted from n = 4 (see B). This follows from the fact that the differences between group retention indices become approximately constant from I(BuO)Si onwards and that the same applies to the correction term (n·d·k) in eqn. 3. The linear relationship is demonstrated in B, Fig. 1 for some homologous series of tetraalkoxysilanes.

In the case of tetraalkylsilanes (see E) the available data are limited. Nevertheless it seems justified to state that for homologous series of tetraalkylsilanes there will exist a linear relationship between retention index and carbon number counted from the third or fourth member in a series.

Pollard et al.[7] have reported a linear relationship between the logarithm of the retention volume and the carbon number for tetraalkylsilanes belonging to the series $R_4Si-R_3SiR'-R_2SiR'_2-RSiR'_3-SiR'_4$ (see E). However, this is true only for certain series. Thus, for the seven series Me_nSiR_{4-n} (R = Et-Am) and Et_nSiR_{4-n} (R = Pr-Am) studied in E, the above statement, which is equivalent to a linear relation between retention index and carbon number, is approximately correct only for the two series Me_nSiEt_{4-n} and Et_nSiPr_{4-n}. For the other five series there will be an increased deviation from linearity with increased difference in size between the two kinds of alkyl groups in the tetraalkylsilanes.

In the case of the corresponding series of tetraalkoxysilanes the same is true, i.e. an approximately linear relationship is found for the series $(PrO)_nSi(OBu)_{4-n}$ but not for the series $(MeO)_nSi(OBu)_{4-n}$ (see B, Fig. 2). The deviation from linearity in certain series of tetraalkyl- and tetraalkoxysilanes is a consequence of the departure from additivity of the group retention indices, as expressed by the correction terms in eqns. 3 and 4.

4. RELATIONS BETWEEN RETENTION INDICES FOR HOMOLOGOUS SERIES OF MIXED TETRAALKOXY- OR MIXED TETRAALKYLSILANES ON THE ONE HAND AND RETENTION INDICES FOR THEIR SYMMETRICAL COUNTERPARTS ON THE OTHER (B, C, E)

When I_{160}^{ApM} for homologous series of mixed tetraalkoxysilanes were plotted against I_{160}^{ApM} for the symmetrical counterparts, the points were found to lie on perfectly straight lines (see B, Fig. 3). In this case there is no deviation from linearity for the three first members in a series as in e.g. the retention index vs. carbon number plots. Similar plots are obtained for I_{160}^{XE}.

For homologous series of mixed tetraalkylsilanes a corresponding linear relationship also exists, although the linearity for some series was inferior to that found for tetraalkoxysilanes (see E, Table VI).

As already discussed in part 2 of the summary, an improved general equation for calculating retention indices of mixed tetraalkoxysilanes from those of their symmetrical counterparts may be derived from the above-mentioned linear relation. This relation may be written

$$I(RO)_xSi(OR')_{4-x} = p_xI(R'O)_4Si + q_x \qquad (6)$$

It appears that, for the three series with x = 1-3, there exists a linear relationship between the p_x-values, and the same is true for the q_x-values

$$p_x = \frac{4-x}{4} + n \cdot k' \qquad (x = 1\text{-}3) \qquad (7)$$

$$q_x = I(RO)_4Si\left(\frac{x}{4} - n \cdot k''\right) \qquad (x = 1\text{-}3) \qquad (8)$$

where n = the combination number.

Accordingly, the six constants (three p_x and three q_x) originally needed to calculate retention indices for mixed tetraalkoxysilanes $(RO)_xSi(OR')_{4-x}$ (x = 1-3) have been reduced to two (k' and k"). For RO = EtO, k' = k" and only one constant is needed. The general equation derived from eqn. 6 for calculating retention indices for mixed tetraalkoxysilanes was given previously (see eqn. 5, part 2). The values of k' and k" for different group combinations, columns and stationary phases are presented in

C, Tables IV and V. (RO in these tables is the smallest group in a combination).

In the linear relation valid for mixed tetraalkylsilanes (equivalent to eqn. 6) there are no relations similar to those in eqns. 7 and 8 among the three p_x-values nor the three q_x-values. On that account no reduction of the number of constants (six) needed to calculate retention indices for mixed tetraalkylsilanes belonging to the three homologous series $R_xSiR'_{4-x}$ (x = 1-3) is possible, and no general equation like eqn. 5 may be derived in this case.

5. TWO-PHASE PLOTS FOR RETENTION INDICES MEASURED ON A NONPOLAR STATIONARY PHASE (APIEZON) AND A POLAR PHASE (XE-60) AND TWO-TEMPERATURE PLOT FOR RETENTION INDICES MEASURED ON APIEZON L (B-E)

Two-phase plots in which retentions measured on nonpolar stationary phases are plotted against retentions obtained on polar phases have become a valuable tool for the identification of organic compounds by gas chromatography. Originally they were mainly utilized for the distinction of classes of compounds *e.g.* alkanes, alkenes, aromatics. However, with increased precision in the retention data measurement, the two-phase plot has also successfully been applied to the identification and differentiation of compounds within one and the same class[8]. In the present case the application of the two-phase plot method to retention data for tetraalkoxy- and tetraalkylsilanes has provided some interesting results.

Two-phase plot for normal tetraalkoxysilanes (B). In the two-phase plot of I^{ApM}_{160} *vs.* I^{XE}_{160} for normal tetraalkoxysilanes, two main linear relations exist (see B, Fig. 4). The first one refers to so-called homologous lines, which connect points in homologous series of tetraalkoxysilanes. Four homologous lines are drawn in Fig. 4 for the series with the formula codes 111X, 112X, 122X and 222X. The formula code simply denotes the alkoxy groups bonded to the silicon atom: 1 = MeO, 2 = EtO, 3 = PrO, etc. The linear relation in homologous series is partly a consequence of the previously established linear relation between the carbon number and I^{Ap}_{160} or I^{XE}_{160}.

The second linear relation in Fig. 4 was more unexpected and refers to so-called structure lines. It appears that these structure lines connect points having the same structure code. The structure code is written a-b-d-e where a, b, d and e are the number of CH_3, CH_2, CH and C groups, respectively. Since all alkoxy groups are normal, d and e are always equal to zero. Along each structure line the tetraalkoxysilanes, all of equal molecular weight, are arranged according to decreasing formula code. Furthermore, the compounds belonging to the same structure series are grouped together with interspaces between the groups in a way which means that the compounds are eluted according to decreasing symmetry.

Two-phase plot for tetraalkoxysilanes containing branched alkoxy groups (D). In order to examine whether the structure group rule discussed in the previous section was also applicable to the structurally more complicated tetraalkoxysilanes with branched alkoxy groups, I_{160}^{ApL} was plotted against I_{160}^{XE} for some members of the two structure groups with the codes 5-4-1-0 and 6-4-2-0 (see D, Fig. 1). The points are seen to lie on straight lines. Thus, it appears that the structure group rule also applies to tetraalkoxysilanes with certain branched alkoxy groups, viz. i-PrO, i-BuO and s-BuO.

Two-phase plot for tetraalkylsilanes (E). The two-phase plot of I_{160}^{ApL} vs. I_{160}^{XE} for tetraalkylsilanes presents quite another picture than the analogous plot for tetraalkoxysilanes. Thus, the spread between the lines is almost zero and all points are well collected along a single straight line. The reason for this is the low polarity of the tetraalkylsilanes. However, a closer inspection to ascertain possible relationships between retention indices for members belonging to the same structure group, revealed linear relations for certain compounds within a structure group (see E, Fig. 2). This is in contrast to the case for normal tetraalkoxysilanes where one linear relationship includes all members in a structure group.

For the structure group investigated (4-6-0-0), two main linear relations exist. The first one (diagonal lines) concerns tetraalkylsilanes belong-

ing to two series with the compounds 1117 and 1135, respectively, as the first members. From these, other members are formed by the systematic transfer of a CH_2 group from an alkyl group larger than Pr to Me. The second linear relation (intersecting lines) refers to three series which are formed from the first compound by transfer of a CH_2 group from Pr to another Pr or to a group larger than Pr, or between two groups larger than Pr. The significance of these linear relations is that there exists a constant relation between the change in I^{ApL}_{160} and in I^{XE}_{160} for a CH_2 transfer in each series. Since only one structure group has been studied, more data are needed to answer the question about the generality of these linear relations. It should also be pointed out that because of the small differences between I^{XE}_{160} and I^{ApL}_{160}, rather precise measurements of retention indices are necessary in order to establish these relations.

Two-temperature plot for normal tetraalkoxysilanes (C). Two-temperature plots are used in addition to, or as substitute for two-phase plots[9]. In this instance retentions measured at two different temperatures on the same stationary phase are plotted against each other. To study the utility of a two-temperature plot for the identification of normal tetraalkoxysilanes, I^{ApL}_{160} were plotted against I^{ApL}_{140} for some compounds (see C, Fig. 3). Comparison with B, Fig. 4 shows that tetraalkoxysilanes with the same structure code align themselves along straight lines in the same way and the same order as in the two-phase plot. However, the spread between the structure lines is considerably less than in the two-phase plot and the precision required in the retention index determination is higher in this case. Accordingly, capillary columns should be used.

6. RELATIONS BETWEEN RETENTION INDICES FOR TETRAALKYL- AND TETRAALKOXYSILANES (E)

Several linear relationships exist between retention indices for homologous series of mixed tetraalkylsilanes on the one hand and retention indices for tetraalkoxysilanes on the other. Thus, eqn. 9 gives the relation between retention indices for mixed tetraalkylsilanes and reten-

tion indices for the corresponding tetraalkoxysilanes

$$I(R_xSiR'_{4-x}) = k_1 I(RO)_xSi(OR')_{4-x} + l_1 \qquad (9)$$

In this expression, R and x are the same throughout a series while the R'-groups form a semihomologous sequence. See E, Fig. 1, where the full lines represent the relationship in eqn. 9. The broken lines in Fig. 1 demonstrate another linear relationship, viz. that between mixed tetraalkylsilanes $R_xSiR'_{4-x}$ (x = 0-4) and the corresponding mixed tetraalkoxysilanes. In these series one group is exchanged for another in a regular manner.

It was previously shown in part 4 of the summary that a linear relationship exists between retention indices for homologous series of mixed tetraalkoxysilanes, $(RO)_xSi(OR')_{4-x}$, and retention indices for their symmetrical counterparts, $(R'O)_4Si$. Accordingly, it follows from eqn. 9 that the relationship given below will be valid (see E, Table VIII).

$$I(R_xSiR'_{4-x}) = k_2 I(R'O)_4Si + l_2 \qquad (10)$$

The linear relationships discussed above are partly a consequence of the linear relationship between retention index and carbon number. However, the linearity for eqns. 9 and 10 is better in that it also comprises the first members in the series, which is not the case for the retention index - carbon number plots. For compounds on the first part of the curve, the linearity depends on the fact that the retention indices of the two compounds contributing to each point deviate equally from linearity in their respective retention index - carbon number plots.

Retention indices for all types of normal, mixed tetraalkoxysilanes may be calculated with great accuracy by the methods developed in this work, while the method proposed for mixed tetraalkylsilanes is less general (see part 2). In the latter case the equation given (eqn. 4) partly failed for tetraalkylsilanes containing Me groups. On this account the usefulness of eqns. 9 and 10 for such calculations was in-

vestigated. It appeared that eqn. 9 was best suited for the purpose. In E, Table IX, the experimental and calculated (eqn. 9) values are given for some trifunctional tetraalkylsilanes containing Me groups and compared with values obtained using eqn. 4. The superiority of eqn. 9 is obvious. Similar results are obtained for other types of methylalkylsilanes.

7. CALCULATION OF TEMPERATURE DEPENDENCE OF RETENTION INDICES FOR MIXED TETRAALKOXYSILANES AND FOR TETRAALKYLSILANES (B, C, E)

When the retention index concept was first introduced by Kováts, it was stated that one of the advantages of the retention index was its small temperature dependence. However, this statement was founded on a limited amount of data and further investigations have revealed that the temperature increment of the retention index may indeed be considerable in certain instances. This is sometimes a drawback but may also advantageously be utilized for identification and separation purposes (see C, Figs. 1 and 2).

For the two types of compounds studied in this work there is a great difference between the retention index temperature increments for the tetraalkoxy- and tetraalkylsilanes investigated. In the former case, 10 dI/dT is always negative and ranges between -3 and -7 index units for Apiezon L and between -0.5 and -9 index units for XE-60. For tetraalkylsilanes, 10 dI/dT alternates between positive and negative values and is several index units lower than for tetraalkoxysilanes. For several reasons it is of interest to be able to predict the magnitude of 10 dI/dT for a certain compound. How this can be done in the case of tetraalkoxy- and tetraalkylsilanes is outlined below.

Tetraalkoxysilanes. The following equation permits an approximate calculation of the temperature increments of retention indices for mixed tetraalkoxysilanes from the increments for the symmetrical counterparts.

$$10[dI/dT](R_xO)_4Si = \Sigma\{10[dI/dT](R_xO)Si\} \qquad (11)$$

In this expression,

R_x = R, R' etc. (up to four different groups), and the right hand expression denotes group increments, obtained from the temperature increments of retention indices for symmetrical tetraalkoxysilanes by division by four.

As shown in C, Table VI, the agreement between experimental and calculated values is satisfying considering the crude method of calculation used. The results indicate that still better agreement might be achieved for methoxyalkoxysilanes by introducing a correction term in eqn. 11, similar to that in eqn. 3. However, since the error is only of the order of 10%, it has been considered unnecessary.

Tetraalkylsilanes. The group increment method used for tetraalkoxysilanes may also be applied to tetraalkylsilanes, but the error is considerably greater in this instance. A better way of calculating 10 dI/dT for tetraalkylsilanes is given in eqn. 12.

$$10[dI/dT](R_4Si) = k_3[I(R_4Si) - 100C_x] + 1_3 \qquad (12)$$

In this expression,

C_x = the carbon number of the tetraalkylsilane R_4Si.

Eqn. 12 means that the sign and magnitude of the retention index temperature increment for a tetraalkylsilane is a linear function of the difference between its retention index and the retention index for the n-alkane with the same number of carbon atoms. Three linear equations must be used in order to cover the tetraalkylsilanes included in this work (see E, Table V). One is valid for symmetrical tetraalkylsilanes, one for mixed tetraalkylsilanes with Me groups and a third equation for mixed compounds without Me groups. The mean deviation between experimental and calculated values for 10 dI/dT by this method is 0.17 index units for both columns. For individual values, see E, Table IV.

8. CALCULATION OF BOILING POINTS FROM RETENTION INDICES (B, E)

From a strictly theoretical point of view there exists a linear relation-

ship between boiling point and retention index for homologous series of compounds, provided that certain conditions regarding activity coefficients and Trouton's constants are fulfilled (see e.g. ref. 10 p. 47). However, in practice plots of retention indices against boiling points for homologous series of compounds are almost invariably curved over a larger range. That this is the case even for n-alkanes is evident from E, Fig. 3.

In the present case, the fact that boiling points have been available only for a limited number of compounds has prevented a more extensive investigation of the relationship between boiling point and retention index for tetraalkoxy- and tetraalkylsilanes. For the tetraalkoxysilanes tested the Kováts' relation

$$\delta T \approx 0.2\delta I \qquad (13)$$

was found applicable to the calculation of boiling points from I_{160}^{ApM}. Here δT denotes the difference between the boiling points of two tetraalkoxysilanes and δI the difference between their retention indices (see B, Table VII). In the case of tetraalkylsilanes, the curved line obtained on plotting I_{160}^{ApL} against boiling points could be approximated by two linear relationships according to eqn. 14 (see E, Fig. 3).

$$t(^{\circ}C) = k \cdot I_{160}^{ApL} + l \qquad (14)$$

The first linear range covers the retention indices 400-850 and the second linear range the retention indices 900-1200. These equations permit the calculation of the boiling point to about 1°C. A serious drawback in boiling point - retention index correlation is the lack of reliable micro methods for boiling point determination, especially above 200°C where existing methods may give large errors.

9. USE OF REFRACTIVE INDEX IN CONJUNCTION WITH KOVÁTS' RETENTION INDEX FOR THE IDENTIFICATION OF ORGANOSILICON COMPOUNDS (F)

The importance of refractive index for identification purposes has undergone a steady decrease since the time when the molar refraction was

used in structural investigations of organic compounds. The reason for this is undoubtedly that a mere refractive index does not reveal much about the structure. Accordingly, the refractive index is hardly used nowadays despite the fact that it is one of the most easily obtainable physical constants and is tabulated for a vast number of organic compounds. It was thought that by combining the refractive index with another easily obtainable physical quantity, its utility for identification purposes would be considerably increased. For several reasons the choice fell on Kováts' retention index, which is also easily arrived at and extensively tabulated. Here the use of the two quantities for the identification of some organosilicon compounds is discussed. However, their combined application is not limited to this type of compound, but has a general utility in organic identification work.

A convenient way of utilizing two physical quantities is to plot them against each other. In order that the graph be easily interpretable, it is desirable that the two quantities are linear with each other for homologous series of compounds. This is unfortunately not the case for the refractive index and the retention index. However, it was found that the refractive index could be converted to a quantity called refractive number (N_D^{20}), which was linear with the retention index. The refractive number is obtained by linear interpolation between refractive indices of n-alkanes, the refractive numbers of which are defined as 100 times their carbon number. Thus, the refractive number of n-pentane is equal to 500, of n-hexane 600, etc. The refractive number of a compound A whose refractive index is $n_D^{20}(A)$ is obtained from the following equation

$$N_D^{20}(A) = 100p + 100 \frac{n_D^{20}(A) - n_D^{20}(C_p)}{n_D^{20}(C_{p+1}) - n_D^{20}(C_p)} \qquad (15)$$

where C_p and C_{p+1} denote two n-alkanes with the carbon numbers p and p+1, between the refractive indices of which $n_D^{20}(A)$ lies. The refractive number is linear with the carbon number for homologous series of compounds with the exception of the one or two first members in a series

(see F, Fig. 1 and Table II). This linear relationship permits the calculation of refractive numbers and consequently refractive indices for missing members in a homologous series.

For mixed tetraalkoxysilanes, another way of obtaining refractive numbers exists. It appears that the methods previously developed for the calculation of retention indices for mixed tetraalkoxysilanes from retention indices for the symmetrical counterparts are also applicable to refractive number calculation (see part 2, eqns. 3 and 5).

$$N_D^{20}[(RO)_4Si] = \Sigma N_D^{20}(ROSi) + \text{correction term} \qquad (16)$$

$N_D^{20}(ROSi)$ = group refractive number, obtained from the refractive numbers for symmetrical tetraalkoxysilanes by division by four. The correction term may be calculated according to the principles described in connection with the retention index calculation, i.e. either as $\Sigma(n \cdot k_1 \cdot d)_{RO-RO}$ or as $\Sigma(n \cdot k_2 \cdot \Delta N_D^{20})_{RO-RO}$. Here n is the so-called combination number, k_1 and k_2 constants, d and ΔN_D^{20} carbon number difference and refractive number difference, respectively, between combined alkoxy groups. A comparison between experimental and calculated values is presented in F, Table III.

N_D^{20} vs. I_{160}^{ApM}. The linear relation between refractive number and retention index follows from the fact that the two quantities separately are linear with the carbon number. However, the extent of linearity is better than in the corresponding carbon number plots (see F, Fig. 2 and Table IV). The refractive number - retention index plot is intended as a tool for the identification of organosilicon compounds. It is seen that the spreading of the lines in the graph is good; also for the tetraalkylsilane series $MeSiR_3$, Me_2SiR_2, Me_3SiR and SiR_4, for which the separation in the two-phase plot was insignificant.

Refractive retention (R_R). A composite quantity, called refractive retention, may be formed from the refractive number and the retention index

$$R_R = \frac{N - I}{I} \cdot 100 \qquad (17)$$

It appears that the refractive retentions for members in homologous series attain characteristic values, which may be utilized for identification purposes (see F, Fig. 3 and Table I).

10. IDENTIFICATION OF TETRAALKOXY- AND TETRAALKYLSILANES BY GAS CHROMATOGRAPHY AND REFRACTOMETRY (B-F)

Compounds belonging to the two types of silanes may be recognized by several methods. Tetraalkoxysilanes may easily be distinguished from tetraalkylsilanes by their ΔI-values, which lie approximately between 140 and 270 (normal compounds) for the former type and between 10 and 30 for the latter. For tetraalkoxysilanes containing branched alkoxy groups the ΔI-values may be considerably lower, but they do not coincide with the values for tetraalkylsilanes (see D, Tables I and II). The refractive retention may also be of value for this purpose (see F, Table I). A third quantity which may serve to discriminate between these compounds is the temperature dependence of the retention index ($10dI/dT$). In the case of the tetraalkoxysilanes this magnitude is always negative and lies between about -2 and -8, while for tetraalkylsilanes it is positive or negative and generally below 2.

Most convenient for the identification of individual tetraalkoxysilanes is undoubtedly the two-phase plot in B, Fig. 4 (see also D, Fig. 1). In many cases it will be possible to pick out a compound with great certainty with the aid of the homologous lines and structure lines in the graph. The ΔI-values are also useful for individual identification of tetraalkoxysilanes since several series, e.g. the series $(MeO)_3SiOR$, $(MeO)_2Si(OR)_2$ and $MeOSi(OR)_3$, may be distinguished on the basis of this quantity (see B, Fig. 5). The refractive number - retention index plot in F, Fig. 2 is of limited value in this connection since all compounds tend to crowd around one and the same line. Finally, chemical methods, e.g. hydrolysis, combined with gas chromatographic investigation of the alcohols formed, may be employed.

The individual identification of tetraalkylsilanes solely on the basis of gas chromatography is a more difficult task. The reason for this is their low polarity, which makes the spreading of homologous lines in the two-

-phase plot very small and causes the ΔI-values to range over a small interval. However, some use may be derived from the ΔI-values, at least for the division of tetraalkylsilanes into subgroups (see E, p. 14). It appears that the refractive number - retention index plot presents the best means for distinguishing different types of tetraalkylsilanes along with the refractive retention (see F, Figs. 2 and 3). It should also be noted that the various methods developed in this work for the calculation of retention indices for tetraalkoxy- and tetraalkylsilanes may be utilized for identification purposes. The same is true of the methods worked out for the calculation of the temperature dependence of retention indices.

The previous discussion has demonstrated the various gas chromatographic means at our disposal for the identification of organosilicon compounds. However, it should be observed that most methods are not specific for these types of compounds but have a general applicability to all types of organic compounds.

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